Metals Materials And Processes, 2000, Vol. 12, No, 2 & 3, pp. 97 - 126.

CHALCOGENIDE GLASSES - AN OVERVIEW

Sudha Mahadevan and A. Giridhar
Materials Science Division,
National Aerospace Laboratories, Bangalore 560 017, India.

(Received 10 January 2000)

Abstract : A brief introduction on the technological importance of chalcogenide glasses is followed by a discussion of the models such as the Random Covalent Network Model, the Chemically Ordered Network Model and the Topological models, which are adopted to understand the atomic arrangement in network glasses. The merits and drawbacks of these models have been pointed out by considering the property-composition dependencies of several chalcogenide glass systems. The importance of considering the effects of chemical ordering and also of network topology in accounting for the features observed in the property-composition data of several systems has been demonstrated, thereby establishing the coexistence of these two effects in chalcogenide glasses. This idea has been applied to separate out the contributions from chemical ordering and network topology, to a fundamental structure sensitive property, namely, the Mean Atomic Volume. Several aspects of the macroscopic characterisation and the effects of metallic additives to chalcogenide glasses are also discussed.

Key Words : chalcogenide glasses, chemical ordering, topological effects, coexistence of effects, effects of metallic additives.

1. INTRODUCTION

Amorphous substances encompass a wide range of materials such as thin films and bulk glasses made of tetrahedrally bonded materials, lone pair semiconductors, oxide glasses, chalcogenide glasses, ionic glasses, dielectric films, metallic glasses etc. Associated with these broad class of materials are also a wide range of properties exhibited by them.

Various techniques, namely, thermal evaporation, sputtering, glow discharge decomposition, chemical vapour deposition, melt quenching are all used for producing amorphous materials; of these, the melt quenching method (where the amorphous solid is formed by the continuous hardening i.e. increase in viscosity of the melt) yields glasses, which are characterised by a well defined transition temperature, referred to as the glass transition temperature (T_g). Glasses thus form a distinctive class of amorphous materials in that they are prepared via a melt route; It can therefore be said that all glasses are amorphous, while all amorphous materials are not necessarily glasses. The fast cooling necessary for the glass formation is generally achieved by quenching in air, water, iced water, iced brine, liquid nitrogen, etc., and in case of metallic glasses, by splat cooling.

Properties such as Infrared transmission, switching, semiconduction, photoconductivity etc., exhibited by many chalcogenide glasses, have rendered these materials technologically important. Some of their applications are as threshold and memory switches, as photoresists, as acousto optic modulators, as infrared transmitting and detecting elements through various optical components and optical waveguides, particularly for the middle infrared region. Characterisation of these materials by probing their physical, thermal, electronic, mechanical and optical properties is important not only for assessing the suitability of specified chalcogenide glasses for the various applications cited above, but also from a more fundamental point of view to understand the nature of the glassy state of matter.

An important feature of muticomponent chalcogenide glasses is the composition dependent tunability of their various properties. For any specified system, the properties

are composition dependent and therefore exhibit a range of values for the various parameters. This aspect is particularly useful as it enables one to choose a desired composition (from within a specified system), which has the required values of the various parameters for specific applications. Further, for any specified system, in the variation of the properties with composition, features such as an extremum, or a change in slope or a kink are generally observed at specific compositions. Correlation of the features observed at specific compositions of various systems, with the atomic arrangement in these materials gives an insight into the nature of the amorphous materials in general, and of the glassy state in particular. For example, studies on the composition dependence of the mean atomic volume (V), elastic properties and the glass transition temperature (T_g) are helpful in understanding the packing of atoms, the nature of bonding and their structural arrangement.

It was originally thought that amorphous materials are structureless (in the sense the word structure is used for crystalline materials), till it was pointed out by Ioffe and Regal[1] that the amorphous materials retain their semiiconducting properties in spite of the lack of long range order, only when the non-crystalline phases retain the short range order of the corresponding semiconducting crystals. It is now well known that a wide range of sophisticated experimental techniques such as x-ray diffraction, small angle x-ray diffraction, neutron diffraction, electron diffraction, extended x-ray absorption fine structure (EXAFS), x-ray photoelectron spectroscopy (XPS), IR and Raman spectroscopy, NMR, ESR, Mossbauer spectroscopy etc., are all being employed to probe into the structure of amorphous materials. The various techniques used for the experimental determination of structure will not be discussed here, but instead, the various models, namely, the Random Covalent Network Model (RCNM), the Chemically Ordered Network Model (CONM), the Constraints Model and the structural transitions model, which are adopted to understand the property-composition dependence of chalcogenide glasses will be briefly reviewed. An elaborate treatment of these models is beyond the scope of this article and specific papers have been cited for further details. Effort has been made to include many key references pertaining to the macroscopic characterisation of chalcogenide glasses, but the emphasis is on the work carried out in the past two decades on chalcogenide glasses at the National Aerospace Laboratories.

2. THE (8-N) RULE

The (8-N) rule, where N is the number of valence electrons, establishes the coordination number, which, for covalent networks corresponds to the connectedness. Thus, the chalcogens (S, Se, Te), with N equal to 6 have a coordination of 2, while Ge and Si which have N of 4, have a coordination of 4.

The IR and Raman spectroscopic studies in glasses have contributed significantly to the understanding of the atomic arrangement in glasses. The amorphous semiconductors are linked together by the same type of chemical bonds and exist in geometric configurations similar to that found in any of the different crystalline polymorphs. Therefore, a comparison of the IR and Raman spectra of the amorphous semiconductors and those of the corresponding crystalline polymorph will yield information about the amorphous phase. In the localised molecular model of interpreting the vibration spectra, some structural elements or units are isolated in the glass and are assumed to vibrate as independent molecules or units. Of course, the units are not completely free and the boundary conditions may somewhat change the vibrations and shift their frequencies; but if the same structural units are present in both the crystalline and amorphous phases,

their vibrational frequencies can be identified. Consistent with the (8-N) rule for the composition dependence of the bond types, two models, namely, the RCNM and the CONM have been developed[2,3] which are briefly outlined below.

3. THE RANDOM COVALENT NETWORK MODEL

This model treats the distribution of covalent bonds as being purely statistical, determined only by the local coordinations and concentrations. Effects leading to preferential ordering such as the relative bond energies are overlooked. A simple covalent binary alloy A_xB_{100-x}, (where x is the atomic percent) with A and B belonging to periods a and b of the periodic table, will have coordinations of (8-a) and (8-b) respectively. In general, there can be A-A, A-B and B-B types of bonds in an alloy of any composition. RCNM allows A-A, A-B and B-B bonds (i.e. both homopolar and heteropolar bonds) at all compositions except at x=0 and x=100. The RCNM has been found to predict accurately the peak area of the radial distribution function curves for several Ge based chalcogenide alloys[4-8]. But this model cannot account for the feature of an extremum or a change in slope in several properties exhibited at the so called stoichiometric composition or the chemical threshold compositions of various systems.

4. THE CHEMICALLY ORDERED NETWORK MODEL (CONM)

In the CQNM [which is also sometimes referred to as chain crossing model or the chemically ordered covalent network model (COCNM)], the formation of heteropolar bonds is favoured over the formation of homopolar bonds. For a glassy alloy A_xB_{100-x}, this model envisages the formation of only the A-B type of bonds for the stoichiometric or tie line compositions[2], which correspond to the formation of stable chemical compounds of the system. These tie line compositions are also referred to as the chemical thresholds of the system[9,10], as they represent compositions corresponding to the chemical compounds.

With the tie line composition of the system as reference, for the A-rich compositions of the system, the CONM envisages formation of A-B type and then the A-A type of bonds. For the B-rich compositions, A-B type and then the B-B type of bonds are formed. The CONM has been very successfully adopted to understand the features observed in the property-composition dependencies of a very wide range of chalcogenide glasses [5, 11-31].

Due to chemical ordering, features such as an extremum, or change in slope or a kink in the property-composition data are observed at the chemical threshold compositions of the various systems. Figure 1 shows the variation of the mean atomic volume (V), the glass transition temperature (T_g) and the electrical conductivity (σ) with composition for families of glasses (with Sb of 5,10 and 15 atomic percent (at. %.)) of the Ge-Sb-Se system[16-18]. The features of extrema seen at specific compositions of the various families of the system have been explained using the CONM[16-18]. According to this model, the glass structure is pictured to be comprised of cross linked structural units of $GeSe_2$ and Sb_2Se_3, with excess Se or Ge dispersed among these units. The extrema in properties seen at the chemical threshold compositions is because these compositions are comprised of cross linked units of $GeSe_2$ and Sb_2Se_3 only, with neither Se or Ge in excess. With the tie line compositions of the various families as reference, a decrease (or increase) in the various properties are seen as one moves to the Se-rich or the Ge-rich compositions of the various families (Fig.1). Though Figure 1 illustrates the data for the Ge-Sb-Se system,

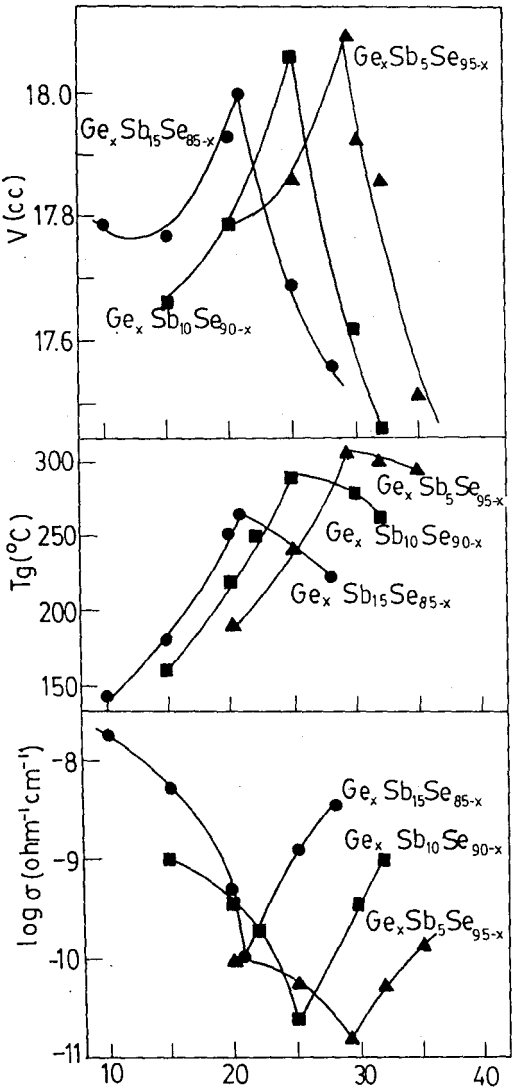

Fig. 1. Data[16-18] of V, Tg and logσ versus atomic percent of Ge for three families of $Ge_xSb_ySe_{100-x-y}$ glasses, with Sb at 5, 10, and 15 atomic percent.

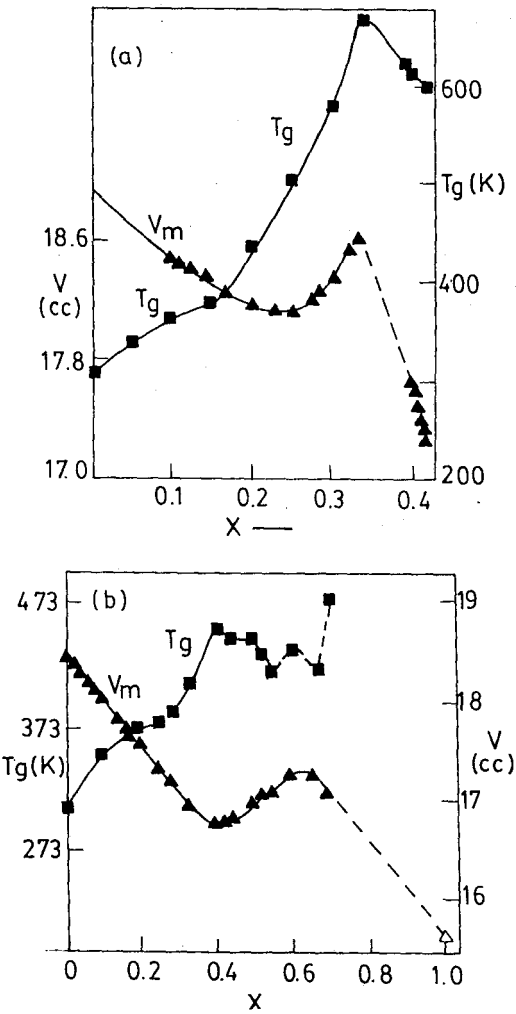

Fig. 2. Data[14,32,33] of V and T_g versus x for (a) Ge_xSe_{100-x} and (b) As_xSe_{100-x} glasses.

have been explained[11-31] using the CONM. similar special features are seen in the physical, thermal, electronic, mechanical and optical properties of several other binary and multicomponent chalcogenide glass systems as well; these features

5. SHORTCOMINGS OF THE CONM MODEL

Though the CONM was successfully adopted to understand features observed in the property-composition data of a wide range of chalcogenide glasses, it was soon realised, that aspects such as the ease of glass formation of specific compositions of many systems and also the greater stability of certain compositions compared to the other compositions of specified systems, were not considered in this model.

Further, with the advent of more efficient preparation techniques, the glass formation regions of several systems could be extended; data on a wider range of compositions in several systems indicated features at compositions in addition to those occurring at the chemical threshold compositions of these systems. Figures 2a and 2b show the variation of V and T_g for the Ge-Se and As-Se systems[32,33]. For the Ge-Se system, in addition to the maxima in V and T_g seen at the composition $Ge_{33.33}Se_{66.67}$ (i.e. the chemical threshold composition, corresponding to the compound $GeSe_2$), features of a minimum in V for the composition ~$Ge_{22}Se_{78}$ and a change in slope in the T_g - composition data at the composition ~$Ge_{17}Se_{83}$ are seen. For the As-Se system similarly, in addition to the extremum in V and T_g seen at the $As_{40}Se_{60}$ chemical threshold composition (corresponding to the compound As_2Se_3), features of a local maximum in V for the composition ~$As_{64}Se_{36}$ and a local peak in T_g at the composition ~$As_{62}Se_{38}$ are also seen.

Various techniques such as x-ray and neutron diffraction, Mossbauer and nuclear magnetic resonance techniques, Raman and Infrared spectroscopic techniques have all contributed to an understanding of the structure of chalcogenide glasses; the results of these studies have been summarised in a recent review [34]. Based on these studies, it is possible to assign three ranges of ordering for the network glasses. Ranges I and II, which correspond to the formation of the basic structural units and their interconnection, represent the short range ordering (SRO) that is present in these materials; this range extends to about 5Å. Range III, which describes the network topology corresponds to the medium range ordering (MRO) that exists in these materials and this extends from ~5 to ~18Å; there is no ordering beyond ~18Å. As the glasses lack long range ordering, it was reasonable to expect that gross topological properties of the resulting network should determine the overall property of the glass, rather than the local chemical ordering of the structural units. This idea led to the development of the topological models of glass structure.

6. TOPOLOGICAL MODELS FOR GLASSES

In these models, the dynamics and the stability of the glass network are given importance. The cross linking in the resulting covalently bonded network is described in terms of the average coordination number, Z. In general, Z is not an integer. It can be regarded as the coordination of a hypothetical psuedoatom forming a structure whose topology is identical to that of the real system[11]. For a binary A_xB_{100-x} composition, Z is given as $Z = [xN_A + (100-x)N_B]/100$, where N_A and N_B are the coordination numbers of the atoms A and B, obtained using the (8-N) rule. The implicit assumption made in using the average coordination number Z is, that it is indiscriminate to the species of the valence bond[35]; thus, it does not distinguish between the homopolar and the heteropolar bonds.

Two topological models, namely, the constraints model[36-39] and the structural transitions model[35] have been developed to discuss the variation of properties with Z. Short range ordering and three dimensional network are considered in the constraints model, while, in the structural transitions model, the medium range ordering and two dimensional layered networks are considered.

6.1 The constraints model

The importance in chalcogenide alloys of the short range bonding interactions described by the valence force fields (VFF) , whose coordinates are the bond vectors connecting

the nearest neighbours was recognised by Phillips and Thorpe[36-39]. The glass forming tendency is maximum when the number of operative mechanical constraints (N_c) experienced by each atom is equal to the number of degrees of freedom (N_d) available to it[36]. In the VFF model, for a binary alloy of the type A_xB_{100-x} , there is one bond stretching A-B interaction (α) and two bond bending β_A(BAB) and β_B(ABA) interactions. Assuming that β_A(BAB) = β_B(ABA), and noting that the bond stretching mode involves two atoms, N_c is written as N_c = (Z/2) + [Z(Z-1)/2], which, when equated to the number of degrees of freedom, 3, of the network, gives a value of 2.45 for Z. A realistic approach which distinguishes between the atoms A and B and their constraints gives a value of Z = 2.40, when the number of operative constraints is equated to the number of degrees of freedom[38]. At Z ~2.40, the glass network is at a mechanical critical point or mechanical threshold at which the rigid regions percolate; the networks which are elastically floppy for Z<2.40, move over to an elastically rigid type for Z>2.40.

Special features observed in the property - Z data around this threshold value of Z ~2.40, have been attributed[9,14,32,33,40-47] to this topological transition, which has been probed by studying both macroscopic (such as the mean atomic volume, the glass transition temperature, elastic modulii, thermal diffusivity, thermal expansion coefficient, optical gap, electrical conductivity, non-reversing heat flow, etc.) and microscopic (such as Infrared, Raman and Mossbauer spectroscopy) techniques. In recent years, important experimental techniques such as the digital data acquisition systems for Raman Scattering and the Temperature Modulated Differential Scanning Calorimetry, have made it feasible to detect details of the rigidity transition; a recent review article[48] discusses the experimental probes pertaining to this stiffness transition in glasses.

Figure 3 shows the schematic of the dependence of V on Z of several chalcogenide glass systems based on the data[35] of several Ge and As chalcogenide glasses with S and Se. In the overall decrease of V with Z, features of a minimum in V for the composition with Z~2.40 and a local maximum in V for the composition with Z~2.67 are observed. The minimum in V at Z~2.40 is traceable to the mechanical threshold, wherein the most stable glass of the system can be expected to have a low volume. Accounting for the feature of a local maximum observed at the composition with Z~2.67, necessitated the consideration of the MRO present in these glasses and the identification of yet another topological threshold at Z~2.67, which is discussed below.

6.2 The Structural transitions model

This threshold was invoked[35] originally for understanding the experimental features associated with the First Sharp Diffraction Peak (FSDP) in diffraction experiments of several chalcogenide glasses. The existence of FSDP and the variation of the FSDP intensity with composition in many chalcogenide glasses are now explicable[35] in the framework of a two dimensional layered structure for these network glasses. In this structural transitions model, the FSDP is interpreted as the peak diffracted from stacks of layers held together by intermolecular bonds consisting of Van der Waals forces. The increase in V between Z~2.40 to Z~2.67 (Figure 3) is traced to the increase in the interlayer separation brought about by expansion of the interlayer distance. In the present context therefore, the compositional changes in this region are regarded as an application of negative pressure[15,35]. The local maximum in V at Z~2.67 in several systems is thus attributed to a structural transition occurring in these glasses, wherein transition to a three dimensional cross linked arrangement from an essentially layered arrangement occurs for compositions with Z>2.67.

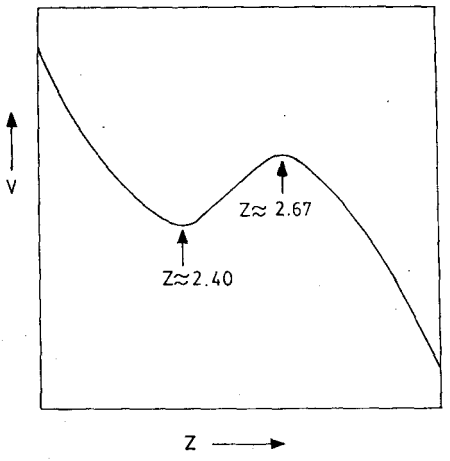

Fig. 3. Schematic of the V versus Z data for chalcogenide glasses based on the V - Z data[35] for a large number of systems.

According to the constraints model, the constraints N_c for an atom can be expressed as $N_c(D,Z)= Z/2+(D-1)(2Z-D)/2$, where Z is the average coordination number and D is the dimensionality[36-39]. It is readily seen by considering the SRO and a dimensionality of 3 (as stipulated by the constraints model) in the above equation, one gets a Z value of 2.40, which is referred to as the mechanical threshold. To understand the threshold at Z=2.67, consideration of medium range structures are necessary. From the above equation, the constraint N_c for an atom included in a planar cluster extending in the xy plane, i.e. for D=2, is given as $N_c=Z/2+(Z-1)$, which, when equated to 3 as per the constraints balancing condition, gives a value of 2.67 for Z.

7. SUCCESS OF THE TOPOLOGICAL MODELS

The occurrence or otherwise of the features at both the topological thresholds depends on the property that is being investigated. The mean atomic volume V is sensitive to both the SRO and the MRO that occur in network glasses. It is therefore reasonable to expect the features of a minimum in V at Z~2.40, a local maximum in V at Z~2.67, with V increasing as Z changes from ~2.40 to ~2.67. This feature is indeed exhibited by many chalcogenide glass systems[14,49-52].In the variation of T_g, the electrical conductivity, the activation energy for electrical conductivity and semiconductor to metal transition pressure of specific systems also, features are seen[14,53] at the compositions which have Z values ~2.40 and ~2.67.

In systems of the type A_xB_{100-x}, containing elements from group V and VI (those containing P, As, Sb, S, Se, Te), the chemical threshold corresponding to the formation of A_2B_3 type structural units occurs at a Z value of 2.40, coinciding thus with one of the topological thresholds. In systems of the type A_xB_{100-x}, containing elements from group IV and VI (those containing Ge, Si, S, Se, Te), the chemical threshold corresponding to the formation of AB_2 type structural units occurs at a Z value of 2.67, coinciding with the other topological threshold. The CONM can account for only one of the features, namely, the one observed at Z~2.40 for the V-VI systems and the one observed at Z~2.67 for the IV-VI systems. The topological models, on the other hand, can account for the features observed at both these Z values. It was therefore thought that the topological models are of a more general nature and therefore they started getting wider acceptance in accounting for the features observed in the property-composition dependence of chalcogenide glasses[35].

8. INADEQUACIES OF THE TOPOLOGICAL MODELS

Though the topological models began to get wider acceptance, some aspects still remained unanswered. The formation of structural units (generally of those of the stable chemical compounds of the respective system) during melt quenching of chalcogenide

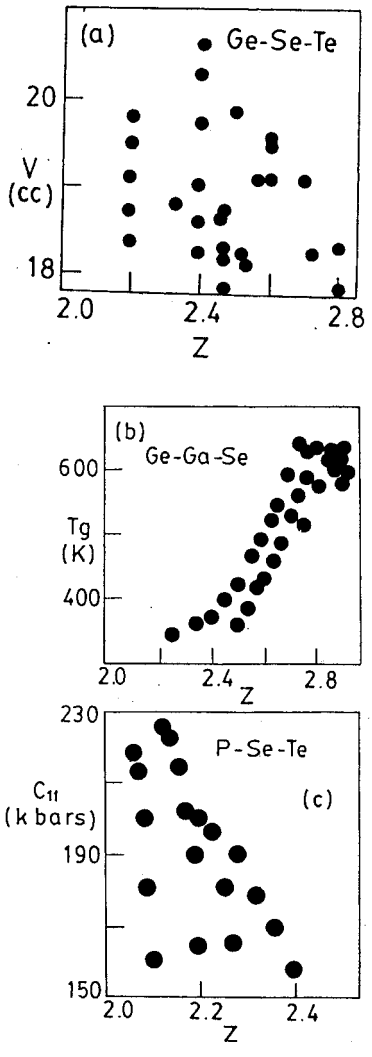

Fig. 4. Data[10,31,66,69] of (a) V versus Z for the Ge-Se-Te (b) Tg versus Z for the Ge-Ga-Se and (c) elastic modulus C_{11} versus Z for the P-Se-Te glasses.

glasses has been established from various spectroscopic and other measurements[11-18,26-30,54-64]; but in the topological models, the role of an atom in contributing to Z only is considered, and the stereochemical aspects of the structural unit formed by these units has been ignored.

The other problem of the topological models is their inability to account for the multiple values observed in the property -Z data at several Z values in many chalcogenide glass systems. In the variation of V, T_g, elastic modulii and several other properties of many chalcogenide glasses, multiple values of these parameters occur at several Z values[10,65-70]. The V-Z, T_g-Z and the elastic modulii C_{11}-Z data of glasses of the Ge-Se-Te, Ge-Ga-Se and P-Se-Te systems are depicted in Figures 4a, 4b, and 4c, wherein it is seen that occurrence of multiple values of these properties at several Z values render it difficult to discern any specific dependence of the property on Z.

The occurrence of multiple values, as already discussed in detail elsewhere[67-72] is due to the effects of chemical ordering, which is also present in these glasses in addition to the topological effects. In binary systems consisting of elements from different groups, each composition has a unique value of Z; therefore the problem of occurrence of multiple values of properties at several Z values does not arise in these systems. In ternary and higher multicomponent systems however, it is possible for a large number of different compositions to have the same specified value of Z. i.e. in these systems, while a specified composition has a unique value of Z, a specified value of Z can be obtained by a large number of compositions within the glass forming region of the system. These different compositions of the system can be expected to have different V (or any other property) because of differences in their structural arrangement, even though they may have the same value of Z. Different fractions of the various types of structural units present in these various compositions (which may have the same value of Z) thus render the property (such as V, T_g, elastic modulii etc.) being different for each composition, thereby resulting in multiple values of the property, at various Z values. The importance of considering at a time the data points of specific families of a system, rather than considering the data points of the system in totality or considering the data points of random compositions of the system, has already been pointed out elsewhere[65,67-69].

9. COEXISTENCE OF CHEMICAL ORDERING AND TOPOLOGICAL EFFECTS IN NETWORK GLASSES

Individually, the topological models or the CONM are not able to account for all the features exhibited by a wide range of chalcogenide glass systems. It is therefore

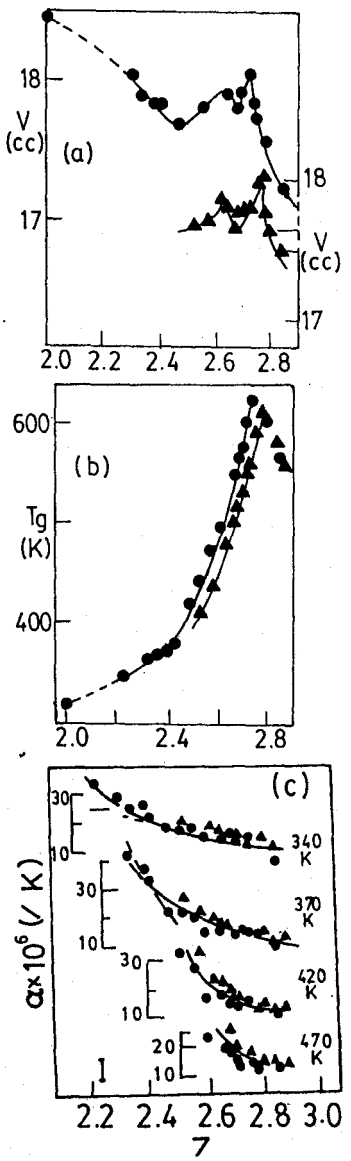

Fig. 5. Data[45,67,68] of (a) V versus Z (b) Tg versus Z and (c) a versus Z for the $Ge_xIn_5Se_{95-x}$ (• data points) and the $Ge_xIn_8Se_{92-x}$ (▲ data points) glasses.

reasonable to expect that these effects coexist in network glasses, with their distinct influences on the property under consideration. In systems containing elements from groups IV, V and VI (i.e. systems with P, As, Sb, Ge, Si, S, Se, Te) , it is not possible to discern the features due to these effects individually because, the chemical thresholds in these systems coincide with one or the other of the topological thresholds. In IV-III-VI systems however, the chemical thresholds of some families have Z values other than the topological threshold values. This is because, while the topological thresholds occur at Z~2.40 and at Z~2.67 for all the systems, the Z values at which the chemical thresholds exist vary from one type of system to another and also from one family to another within a specified system. Investigations on IV-III-VI systems such as the Ge-In-Se, Ge-Ga-Se, As-Al-Te systems[45,67-70] and several other multicomponent systems[26,73] indicated occurrence of features at the chemical thresholds of these systems in addition to those at the topological thresholds.

The V, T_g and the thermal expansion coefficient (α) data[45,67,68] of the Ge-In-Se system are depicted in Figures 5a, 5b and 5c. It is seen (Figure 5(a)) that V exhibits features at both the topological thresholds and also at the chemical thresholds of the two families. The V-Z data of individual families of the Ge-Sb-Se and the Ge-Ga-Se glass systems also have features which can be rationalised by taking the influence of both the topological and chemical ordering effects into account[69,71]. Data on V are available for a large number of binary and ternary chalcogenide glass systems [14,40,49,50,74-80]. All the data display a minimum in V at Z~2.40; in addition, local maxima occur at Z~2.67 and also at the Z values corresponding to the chemical thresholds of the various families in each system. In some cases however, if the chemical threshold composition has a Z value close to ~2.67, the local maximum at the topological threshold of Z~2.67 is not always distinctly seen.

In the T_g data of the Ge-In-Se glasses [Figure 5(b)], a change in slope is seen at the topological threshold of Z~2.40 and peaks in T_g are seen at Z values corresponding to the respective chemical thresholds of the two families; but no distinct feature is seen at the other topological threshold of Z~2.67. The data of Ge-Sb-Se, Ge-As-Se and Ge-Ga-Se systems also show similar behaviour[69,71].

In the α-Z data of the Ge-In-Se glasses (Figure 5 (c)), features are seen at the two topological thresholds, but not at the chemical thresholds of the two families. But in the α-

composition data of the Ge-As-Se and Ge-Sb-Se glasses, clear changes in slope are observed at the respective chemical thresholds of the various families of the systems[66,81].

In the elastic modulii data over a limited range of Z from 2.25 to 2.50 for the As-Sb-Se glasses, features are seen[82] at the composition with Z=2.40; this composition also coincides with the chemical threshold composition of the system. The peaks in density and sound velocities observed for As_xSe_{100-x} glasses at Z = 2.40 have been attributed to chemical ordering than to percolation effects[83]. In the Ge-Sb-Se, Ge-As-S and Ge-Sb-S systems, the elastic modulii are found to be sensitive to the medium range ordering in their networks[80,84,85]. This results in a steep increase in the elastic modulii for compositions with Z>2.67.

From the above observations, it can therefore be concluded that the occurrence or otherwise of features at the two topological thresholds and also at the chemical thresholds of a system depends not only on the system that is being investigated but also on whether the property that is being considered is sensitive to any or all of the short range ordering, the medium range ordering or the chemical ordering present in the respective glass networks. Discussion of the property-composition data of a number of systems corroborate this conclusion[26].

10. TOPOLOGICAL EFFECTS IN THE MEAN ATOMIC VOLUME OF CHALCOGENIDE GLASSES

It is now known that, due to the coexistence of the topological effects and the effects of chemical ordering, multiple values of parameters occur in the property - Z data of many chalcogenide glasses, thereby rendering it difficult to infer any specific dependence of the property on Z for these systems. If it is possible to separate out the contributions from these effects to any property, then it might possible to discern the features due to these effects more clearly. Such an exercise was undertaken[72] for the mean atomic volume (V); in this analysis, by writing the measured mean atomic volume (V_m) as the sum of a component V_{co} (which takes into account the effects of chemical ordering) and a component V_t (due to topological effects), the V_t - Z dependence has been inferred for several chalcogenide glass systems[72]. Taking into account the formation of structural units due to chemical ordering, V_{co} is evaluated as equal to $\Sigma M_i V_i$, where M_i and V_i are the mole fraction and the volume of the individual structural units and elements of which the composition is comprised of ; for each one of the compositions, the summation is carried out over the various types of structural units with heteropolar bonds first, and then excess, if any, of the elements with homopolar bonding . Referring to the original paper for details, it is enough for the purpose of this article to summarise some of the results[72]. Using the analysis, the V_t - Z data was inferred for three types of systems, namely, (i) those in which the topological effects are already observed in the V_m - Z data, (ii) those in which there are no features in the V_m - Z data either due to the topological effects or the effects of chemical ordering, with each effect camouflaging the effect of the other and (iii) those for which multiple values occur in the in the V_m - Z data thereby rendering it difficult to discern any specific dependence of V_m on Z.

Figures 6, 7 and 8 show respectively the V_m - Z and the V_t - Z data for the three types of systems (i), (ii) and (iii) discussed above. For the Ge-Se and As-Se systems, (Figure 6), the topological features of a minimum in V at Z~2.40 and a local maximum in V at Z~2.67, seen already in the V_m - Z data, are also retained in the corresponding V_t - Z data. For the As-Te, P-Se and the Ge-As-Te systems (Figure 7), the topological features are seen

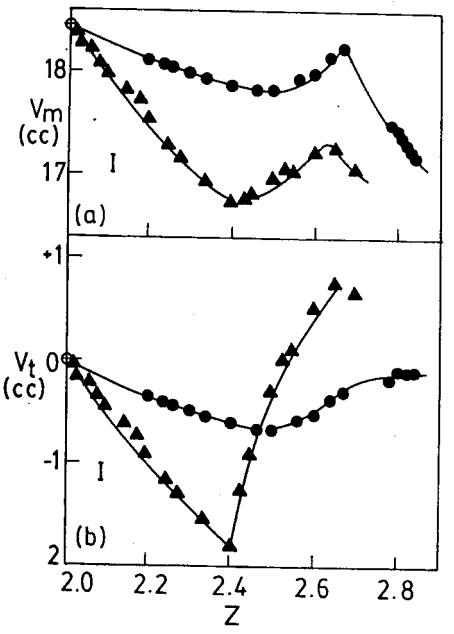

Fig. 6. V_m-Z and V_t-Z data[72] for the Ge-Se (● data points) and the As-Se (▲ data points)

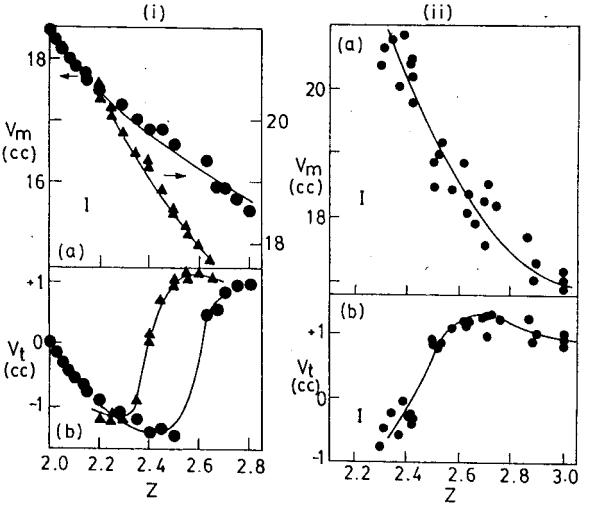

Fig. 7. V_m-Z and V_t-Z data[72] for the (i) As - Te (▲ data points) and the P - Se (● data points) system and (ii) the Ge - As - Te system.

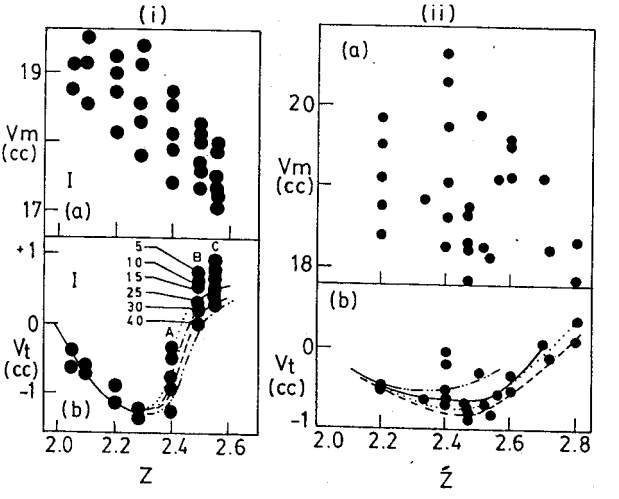

Fig. 8. V_m – Z and V_t – Z data for (i) the As–Se–Te and (ii) the Ge–Se–Te system

only in the V_t - Z data after the effect of chemical ordering (which was camouflaging the topological effects) has been taken care of in V_m. For the As-Se-Te and the Ge-Se-Te systems (Figure 8), the topological effects which could not be clearly seen in the V_m- Z data (due to the occurrence of multiple values of V_m at several Z values), are rendered clearer in their V_t - Z data.

The possibility of separating the V_t - Z data from the V_m-Z data for several systems, indicate that the multiple values of property-Z data seen in several systems is indeed due to the coexistence of the effects of chemical ordering and those due to network topology[72]. The multiple values seen in other properties such as the T_g - Z data and the elastic modulii - Z data are also due to the coexisting effects of chemical ordering. However, separating the individual contributions in these properties is more involved than that compared to V.

In the discussions so far, (sections 1 to 10), though several properties are discussed, the emphasis has been mainly on the mean atomic volume (V). This is because data on V are available on a wide range of systems. Further, being a fundamental structure sensitive property, V lends itself as a probe for checking the validity of various models proposed for the glassy state of matter.

11. MACROSCOPIC CHARACTERISATION OF CHALCOGENIDE GLASSES

In this section, some aspects pertaining to the measurement of macroscopic properties of glasses, namely, the mean atomic volume (V) , the glass transition temperature (T_g), the electrical conductivity (σ), thermoelectric power (S), the elastic properties are briefly discussed along with some precautions that are necessary in the various measurements. Due to features observed at specific compositions in a system, macroscopic measurements on glasses yield more information on the gross structural aspects, compared to those on crystalline materials.

It was originally thought that as glasses are metastable, the various properties for any specified composition are likely to vary from sample to sample and also for samples from different batch preparations of any specified composition. While this may be true for other amorphous materials, the situation is quite different for bulk chalcogenide glasses. If measurements are performed on annealed (i.e. stabilised) samples, it is possible to get parameter values within a narrow range from measurements on a large number of samples from different batch preparations of any specified composition. For annealed samples, the measured parameters taper to a value corresponding to the equilibrium structure of that composition. Annealing is generally achieved by holding the sample for about 30 to 45 minutes at or near the respective T_g and then cooling it.

11.1 Mean Atomic Volume, (V)

V is an important parameter as it is sensitive to the SRO, the MRO and the chemical ordering present in the glasses. Accurate determination of density to better than 0.04%, [performed by hydrostatic methods (using any of the modern analytical balances capable of mass measurement to better than 0.0002 grams) using an appropriate immersion fluid] are warranted to get useful information about a system and to infer differences in V from one composition to another within a system. Utmost care is therefore necessary in density determinations; the accuracy of the measurement is enhanced by avoiding formation of any air bubbles around the samples, by increasing the charge size to typically ~1g or more and also by using large diameter beakers (for the immersion fluid) to minimise edge effects. Table I lists the density data[14,32,40,49,66,70,85-145] obtained on several common elemental, binary and ternary chalcogenide glasses; for any specified composition, the various values from different sources lie within a narrow band of better than 0.5% in most of the cases (and to better than 1%, in the remaining compositions), corroborating that the parameter values lie in a narrow range for the bulk chalcogenide glasses. Also, the density differences between the as prepared and stabilised glasses[110,124] are less than ~0.003gcm^3, which is less than 0.01%, for typical chalcogenide glasses.

11.2 The glass transition temperature (Tg)

T_g is generally measured using a differential scanning calorimeter (DSC) and taken as the temperature corresponding to the intersection of the two linear portions adjoining the transition elbow in the DSC thermogram[146,147]. Powdered samples (typically ~20mg) crimped in the standard aluminium pans provided with the DSC are used for the measurement. The samples are annealed in situ in the DSC set up by first heating them beyond their T_g, holding them at this temperature for about 20 to 30 minutes and then cooling them.; the T_g of the annealed sample is estimated from the subsequent

Table I. Density data of various glasses from different sources

glass	d (g/cc)	Ref.
Se		
	4.288	86
	4.278	87
	4.282	88
	4.280	89
	4.280	90
	4.280	91
	4.281	92
	4.269	93
	4.260	94
	4.280	95
As		
	4.720	96
	4.700	97
	4.700	70
As_2Se_3		
	4.620	88
	4.600	98
	4.580	99
	4.580	100
	4.580	101
	4.580	66
	4.580	102
	4.580	103
	4.580	104
	4.620	14
	4.640	105
	4.600	106
	4.620	107
	4.587	83
	4.686	108
	4.620	91
	4.580	109
	4.588	110
$GeSe_2$		
	4.210	14
	4.250	111
	4.260	32
	4.210	112
	4.220	113
	4.200	114
GeS_2		
	2.710	112
	2.717	113
	2.691	115
	2.720	116
	2.722	117
	2.730	118
	2.700	85
GeS_2 (contd.)		
	2.715	119
	2.700	120
	2.700	121
As_2S_3		
	3.187	66
	3.195	103
	3.180	105
	3.168	85
	3.187	49
	3.182	122
	3.180	121
	3.079	108
	3.200	123
	3.186	124
As_2Te_3		
	5.51	66
	5.54	125
	5.54	126
	5.53	127
	5.54	116
P : Se		
5 : 95	4.230	128
	4.215	66
10 : 90	4.147	66
	4.139	129
15 : 85	4.079	128
	4.068	66
20 : 80	3.968	66
	3.971	129
28.60 : 71.40	3.780	66
	3.810	129
40 : 60	3.548	128
	3.550	66
	3.547	129
50 : 50	3.328	128
	3.310	66
As : Se		
5 : 95	4.326	14
	4.340	83
	4.312	110
4.8 : 95.2	4.330	66
10 : 90	4.370	99
	4.400	66
	4.360	14
	4.361	83
15 : 85	4.392	14
	4.382	83
18 : 82	4.410	14

glass	d (g/cc)	Ref.
As : Se (contd.)		
18.18 : 81.82	4.424	88
20 : 80	4.430	91
	4.450	99
	4.440	66
	4.450	14
	4.413	83
25 : 75	4.480	88
	4.503	14
	4.459	127
28.49 : 71.51	4.536	130
28.60 : 71.40	4.540	66
44.40 : 55.60	4.520	66
43.86 : 56.14	4.520	130
44.44 : 55.56	4.579	88
45 : 55	4.580	91
	4.590	66
	4.586	14
	4.577	83
50 : 50	4.515	88
	4.450	91
	4.500	99
	4.520	66
	4.530	14
Ge : Se		
10 : 90	4.328	83
	4.340	91
	4.359	66
	4.320	14
	4.359	32
	4.295	131
	4.339	40
14.3 : 85.7	4.367	66
	4.320	111
15 : 85	4.360	91
	4.330	14
	4.350	40
	4.349	83
20 : 80	4.370	91
	4.372	66
	4.340	14
	4.330	111
	4.359	131
	4.356	40
	4.361	83
	4.370	107
25 : 75	4.360	91
	4.355	66
	4.340	14
	4.290	111

glass	d (g/cc)	Ref.
Ge : Se (contd.)		
25 : 75	4.347	32
	4.290	131
	4.339	40
	4.330	83
30 : 70	4.281	14
	4.290	83
40 : 60	4.325	66
	4.380	14
	4.360	111
	4.372	40
As : Te		
20 : 80	5.680	66
	5.750	132
25 : 75	5.660	66
	5.700	132
	5.660	133
50 : 50	5.470	66
	5.450	132
	5.360	133
55.5 : 45.5	5.410	66
	5.384	132
Ge : S		
10 : 90	2.200	115
	2.204	117
20 : 80	2.485	115
	2.400	117
	2.438	85
25 : 75	2.587	115
	2.474	117
32 : 68	2.715	115
	2.750	117
35 : 65	2.831	117
35.1 : 64.9	2.775	115
38.1 : 61.9	2.950	115
38 : 62	2.950	117
40 : 60	3.060	115
	3.015	117
	3.069	134
43 : 57	3.200	115
	3.152	117
As : S		
10 : 90	2.283	66
10.47 : 89.53	2.230	49
33.33 : 66.67	2.991	66
33.78 : 66.22	2.947	49
20 : 80	2.585	66
20.79 : 79.21	2.544	49
28.6 : 71.4	2.837	66
29.67 : 70.33	2.797	49

glass	d (g/cc)	Ref.
Se : Te		
20 : 80	4.674	66
	4.670	135
21 : 79	4.680	94
Ge : As : Se		
10 : 10 : 80	4.390	91
	4.362	76
10 : 20 : 70	4.470	91
	4.484	76
10 : 30 : 60	4.510	91
	4.496	76
10 : 40 : 50	4.490	91
	4.485	76
10 : 50 : 40	4.540	91
	4.528	76
12.50 : 25 : 62.50	4.447	136
	4.500	66
20 : 10 : 70	4.410	91
	4.408	76
	4.378	83
20 : 20 : 60	4.410	91
	4.396	76
20 : 30 : 50	4.470	91
	4.436	76
	4.441	137
	4.460	138
20 : 40 : 40	4.550	91
	4.501	76
30 : 10 : 60	4.360	91
	4.343	76
30 : 15 : 55	4.420	139
29.6 : 14.8 : 55.6	4.391	66
30 : 20 : 50	4.470	91
	4.432	76
30 : 30 : 40	4.580	91
	4.503	76
30 : 40 : 30	4.700	91
	4.666	76
40 : 20 : 40	4.597	91
	4.531	76
	4.606	83
	4.531	137
Ge : As : S		
3.80 : 38.5 : 57.7	3.170	85
	3.200	66
16.67 : 33.33 : 50	3.202	85
	3.230	66
37.5 : 37.5 : 25	3.849	85
	3.810	66
33.33 : 33.33 : 33.33	3.792	85
Ge : As : S (contd.)		
33.33 : 33.33 : 33.33	3.940	66
Ge : Sb : Se		
10 : 10 : 80	4.605	131
	4.620	66
	4.610	79
10 : 15 : 75	4.765	66
	4.740	18
10 : 20 : 70	4.904	131
	4.908	66
	4.900	79
10 : 25 : 65	5.043	66
	5.040	79
15 : 5 : 80	4.492	66
	4.480	79
15 : 10 : 75	4.623	66
	4.660	18
	4.620	79
15 : 15 : 70	4.754	66
	4.730	18
15 : 25 :60	5.031	66
	5.040	79
20 : 5 : 75	4.470	66
	4.490	18
	4.500	79
20 : 10 : 70	4.596	131
	4.615	66
	4.570	18
	4.600	79
20 : 15 : 65	4.687	66
	4.690	18
	4.700	79
20 : 20 : 60	4.909	131
	4.892	66
	4.900	79
25 : 5 : 70	4.447	66
	4.450	18
	4.460	79
25 : 10 : 65	4.534	131
	4.533	66
	4.520	18
	4.510	79
25 : 15 : 60	4.748	66
	4.710	18
	4.750	79
30 : 10 : 60	4.625	131
	4.618	66
	4.610	18
	4.620	79

glass	d (g/cc)	Ref.
As : Al : Te		
19 : 5 : 75	5.540	66
	5.546	70
38 : 5 : 57	5.360	66
	5.395	70
47.5 : 5 : 47.5	5.340	66
	5.274	70
Ge : Ga : Se		
10 : 10 : 80	4.473	69
	4.432	140
30 : 10 : 60	4.501	69
	4.504	140
23.5 : 5 : 71.5	4.349	69
23.75 : 5 : 71.25	4.406	140
10 : 5 : 85	4.414	69
10.56 : 5 : 84.44	4.369	140
Ge : In : Se		
32 : 5 : 63	4.483	67
32.75 : 5 : 62.25	4.456	140
16 : 5 : 79	4.506	67
15.83 : 5 : 79.17	4.478	140
As : Sb : Se		
33.33 : 16.67 : 50	4.960	102
	4.961	66
34.48 : 13.80 : 51.72	4.920	102
	4.892	66
Ge : Se : Te		
20 : 60 : 20	4.694	66
	4.700	141
22.8 : 57.2 : 20	4.682	66
23.33 : 56.67 : 20	4.680	141
25.7 : 64.3 : 10	4.503	66
26.67 : 63.33 : 10	4.530	141
As : Se : Te		
40 : 48 : 12	4.773	66
	4.740	142
	4.733	143
40 : 36 : 24	4.973	66
	4.868	142
40 : 30 : 30	5.070	66
	5.079	66
	4.990	142
	4.948	143
	5.068	144
40 : 18 : 42	5.269	66
	5.270	142
40 : 12 : 48	5.371	66
	5.375	142
	5.397	143
40 : 40 : 20	4.915	66

glass	d (g/cc)	Ref.
As : Se : Te (contd.)		
40 : 40 : 20	4.850	142
P : Se : Te		
6 : 54 : 40	4.979	129
	5.000	66
7 : 63 : 30	4.782	129
	4.800	66
8 : 72 : 20	4.580	129
	4.620	66
9 : 81 : 10	4.377	129
	4.410	66
12 : 48 : 40	4.893	129
	4.910	66
14 : 56 : 30	4.704	129
	4.710	66
16 : 64 : 20	4.479	129
	4.450	66
17.15 : 42.85 : 40	4.755	129
	4.800	66
18 : 2 : 80	4.208	129
	4.270	66
20 : 50 : 30	4.557	129
	4.590	66
22.88 : 7.14 : 20	4.339	129
	4.360	66
25.70 : 64.30 : 10	4.087	129
	4.090	66
28 : 42 : 30	4.425	129
	4.370	66
36 : 54 : 10	3.833	129
	3.840	66
Ag : As : Se		
22.22 : 33.33 : 44.44	5.620	66
	5.630	145

thermogram recorded at the desired heating rate. Though all the factors that determine the T_g of a glass have not been completely unravelled[11], the experimentally determined T_g of a glass, by and large depends on (1) the composition [through (a) the optical gap, E_o, and the connectedness, C, as per the T_g - E_o - C correlation[148] (b) the average coordination number[26], (c) mean bond energy[149] (d) sound velocity[150]] (2) the heating rate used in the measurement and (3) the thermal history of the sample. To infer the composition dependence of T_g for a system therefore, the values of T_g at a specified heating rate have to be compared for all the compositions which have similar thermal history. The following procedure is suggested[146] for rendering identical thermal history for the samples. To measure the T_g of a sample at a specified heating rate, say α, the sample is first heated in situ in the DSC set up and taken to a temperature well beyond its T_g. The sample is then cooled through its transition region at the rate α ; the subsequent thermogram, recorded at the heating rate of α is used to infer the T_g of the sample at the heating rate α . With all these precautions, it is found that the scatter in the value of T_g for any specified composition and heating rate ranges from 0.5 to 2K in most cases; for values of T_g ranging from ~300K to 700K for most chalcogenide glasses, this scatter amounts to not more than 0.7%. The activation energy for glass transition is generally estimated[25,151-154] adopting the Kissinger's method [154].

11.3 DC electrical conductivity (σ)

The σ of chalcogenide glasses range[127,156,157] from ~10^{-4} to ~10^{-17} ohm^{-1} $cm.^{-1}$ at 300K , thus spanning from semiconducting to semi-insulating values. Variation of σ of specific compositions with temperature and variation of σ across compositions of any specified system, range from four to eight orders of magnitude depending on the system. Measurement of σ on annealed bulk samples (typically 0.5 to 1mm thick, and area of ~ 0.1 to 0.5 cm^2, with opposite faces rendered parallel) are generally made using the two probe method. The contacts from the sample faces to the electrodes are effected through silver paste. In the constant voltage method [21,158,159], a known voltage (typically 2 to 5 volts) is applied to the sample and the current in the circuit measured with a precision meter capable of measuring picoamperes. Constant current methods, wherein a known current is passed through the sample, and the voltage drop across the sample is measured with a voltmeter (with very high input impedance of ~10^{14} ohms), can also be adopted. For measurements of conductivity less than 10^{-12} ohm^{-1} cm^{-1}, the electometric method[160] of charging and discharging a capacitor is used.

Initial measurements indicated that over a certain temperature range, the σ of chalcogenide glasses follows the activated behaviour of the type $\sigma = C \exp[-\Delta E/2kT]$, (where ΔE is the activation energy for conduction and k is the Boltzmann's constant). Simple chemical considerations, the activated temperature dependence and the optical absorption data all suggested[161,162] a band model with the valance and conduction bands separated by a gap, known as the mobility gap. It is now known that over a wide temperature range, the σ of chalcogenide glasses follows[11,157] the schematic shown in Figure 9. Different conduction mechanisms are operative in the regions (I) to (IV) shown in the Figure 9; various band models such as the Mott-CFO model, Davis-Mott model, Marshall-Owen model have all been developed[11,157,163] for the electronic bands in amorphous materials and to account for the observed σ vs. 1/T data of various chalcogenide glasses. Discussions of the various conduction mechanisms and of these models are beyond in the scope of this article.

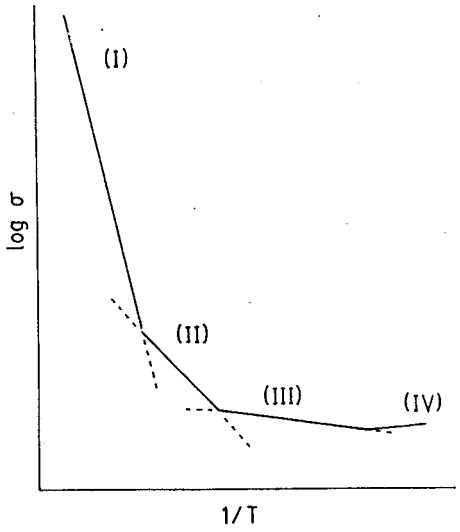

Fig. 9. Schematic[157] of the logσ versus 1/T data over a wide range of temperature for chalcogenide glasses

11.4 Thermoelectric Power

Thermoelectric power or the Seebeck coefficient, S, is an important transport property, which, in conjunction with σ measurements can help decipher the mechanism of conductivity in the material. Also, the slope of the S vs.1/T data gives the activation energy for S or the mobility gap. Typically, rectangular samples (5 to 6 mm long, 2mm to 3 mm broad and of 2 mm thick) with platinum leads fused to its ends are used for the measurement of S. Figure10 shows the block diagram[164] of a typical set up, in which the sample is held in the well formed between two identical metal blocks well insulated from each other. A few turns of nichrome wire on one of the metal blocks (with a few volts applied to it) serves to maintain one end of the sample about three to four degrees higher than the other end to generate the thermopower. For measurement of variation of S with temperature, this assembly is introduced into an appropriate furnace. The high impedance of the chalcogenide samples necessitate that the input device in the amplifier (used to amplify the thermopower generated) has a high input impedance of the order of 10^{12} or 10^{14} ohms; moreover, for typical thermopower values ranging from 0.5 to 2 mV/°K, it is necessary that the bias current of the input device of the amplifier is in the range of fraction of a picoampere. Thus, for measurement of a thermovoltage of 2mV developed across sample impedance of 10^{10} ohms, the input device, in addition to having an input impedance $>10^{12}$ ohms, should also have a bias current < 0.02 picoamperes. Unless these conditions are satisfied, the amplifier will register some stray voltage or noise voltage instead of the actual thermopower. Discussions of S vs. 1/T data and the σ vs. 1/T data using the single carrier model and the two carrier model can be found in the literature[156,162,165-167].

11.5 Elastic Constants

The elastic modulii, namely, the Youngs modulus (E), the shear modulus (G), the bulk modulus (K) and the Poisson's ratio (p), are calculated from standard expressions using the measured values of the longitudinal sound velocity (C_l), the transverse sound velocity (C_t) and the density d of the material. The pulse superposition technique[168] or the pulse echo overlap technique[169,170] are generally used[82,84,171] to determine the sound velocities in glasses. Cylindrical samples about 8 to 12 mm diameter, 4 to 6 mm thick with the end faces rendered absolutely parallel (to wedge angle better than 0.2sec., using a special lapping-polishing jig) are used for the velocity measurement[82,84]. A short duration pulse of ultrasonic waves (typically 10MHz.) is generated by exciting a piezoelectric quartz transducer which is bonded to one of the faces of the sample. The waves undergo multiple reflection from the end faces of the sample and the same transducer detects the echoes. The transit time of the echo in the sample is measured by using a frequency counter as described in detail elsewhere[82,84,171].

As pointed out earlier[84], for crystalline compounds, a relationship of the form K = constant x V^{-m}, holds good between the bulk modulus and the mean atomic volume V; m is 4/3 for

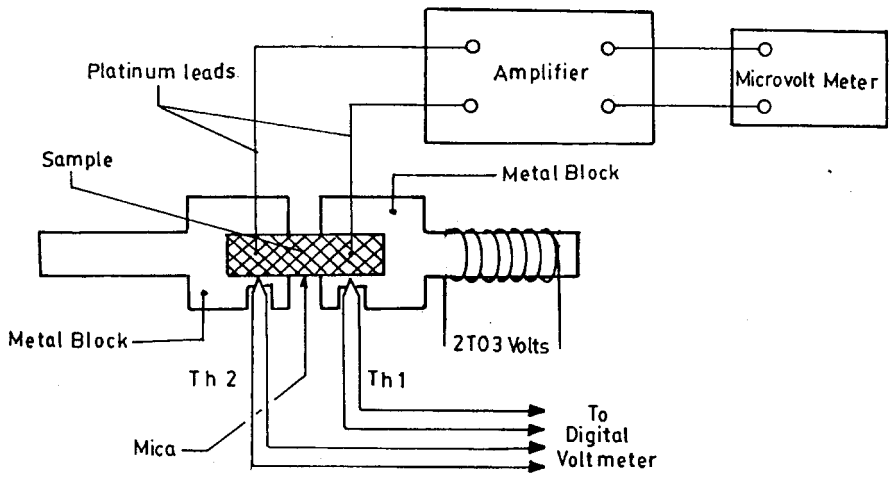

Fig. 10. Block diagram of a typical[164] Thermoelectric power measuring set up.

a wide range of materials and is of the order of 4 to 5 for elements. The situation is not simple in glasses and a wide range of behaviour is seen; while alkaline earth glasses follow the above equation with m = 4/3, several oxide and chalcogenide glasses have a value of m of 4 or 6. In several other glasses, the trend of the K versus V dependence is itself reversed and glasses of smaller volume have smaller bulk modulus than glasses of larger volume. A closer examination of these data have indicated[84] that in addition to volume, the type of bonding also has a great influence in determining the bulk modulus of glasses.

11.6 Thermal Expansion Coefficient (α)

α is generally measured using any of the commercially available dilatometers, which measure $(\Delta \ell)/\ell$ as a function of temperature.; here, ℓ is the initial length of the sample and $\Delta\ell$ is the change in length due to expansion. Samples are cut into rectangular sections of typically 4 to 8 mm in width and 8 to 15 mm in length, depending on the piece available in the glass synthesis ampoule. The end faces normal to the length of the sample are rendered smooth and absolutely parallel using a hand polishing jig. It is important that the samples are well annealed before measurement, as otherwise they register an apparent contraction near about the corresponding Tg, during the measurement. This apparent contraction disappears in the subsequent runs on the sample as the sample gets annealed during the run.

Using the relationship $\alpha = (1/\ell)\ (\Delta\ell/\Delta T)$, α is calculated at any temperature from the slope of the $(\Delta\ell)/\ell$ versus T data. It is possible to estimate the T_g, the softening temperature T_s and the change $\Delta\alpha$ in the expansion coefficient α during the glass transition, from a dilatometric data[65] as depicted in Figure 11. The change in free volume during glass transition, V_f, is given as $3\Delta\alpha T_g$. Data on several glass systems has indicated[65] that chalcogenide glasses are not necessarily in a state of iso-free volume during transition.

12. METALLIC ADDITIVES IN CHALCOGENIDE GLASSES

It was thought for a long time that amorphous semiconductors could not be doped because of the following two reasons (i) any foreign atom introduced into an amorphous matrix would take up its normal chemical valence because of the supposed flexibility of

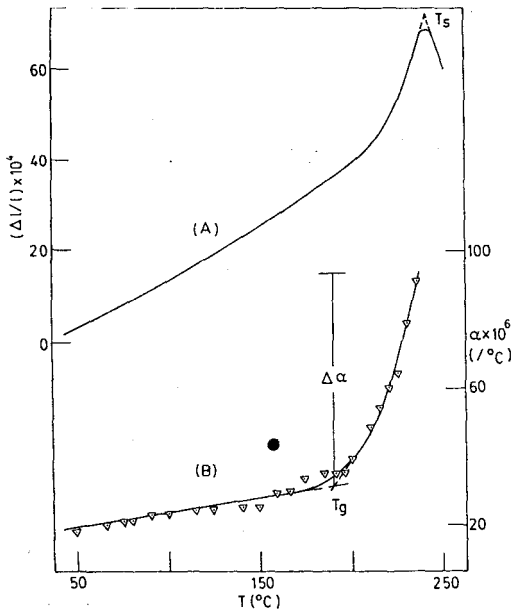

Fig. 11. (a) Plot of $(\Delta l)/l$ versus T and (b) α versus T for a $Ge_{23.33}Se_{61.67}Te_{15}$ glass[65], indicating T_g, T_s and $\Delta\alpha$

the random network which is conducive to satisfy the local coordination and (ii) the density of states in the gap is sufficiently large so that the Fermi level does not shift by the addition of electrons or holes by the impurity atom. The possibility of doping these materials was first demonstrated[172,173] in amorphous hydrogenated Si; for doping without hydrogen, large impurity concentrations were required[174-176]. In these studies, the term modifier or additive is used for the metal atoms introduced; this is because, compared to the conventional dopants in crystalline semiconductors (in which one is considering metallic materials in ppma levels), the modifiers or additives are in much larger amounts ranging from a few atomic percent to sometimes as high as 20 to 30 atomic percent. Interesting electronic effects observed in chalcogenide glasses are (i) the role of various metals such as Cu, Ag, In, Ga etc., in small amounts (generally up to 1 to 2 at. %). (ii) chemical modification of several chalcogenide glasses by introduction of larger quantities of certain metals and (iii) transformation in the type of electronic conductivity from the generally observed p type to n type on addition of metals such as Bi, Pb etc. An understanding of these effects involves a knowledge of the electronic structure of these materials in terms of the charged defect states; a discussion of these aspects is beyond the scope of this article and references [176 to 196] dwell upon these topics. Much of the work has thus been restricted to the effects of metallic additives on the electronic and photoconducting properties of chalcogenide glasses.

In general, the additive in a multicomponent glass can affect their spatial, structural, chemical and electronic properties. Their effect can therefore be probed not only by studying the electrical conductivity, but by a careful characterisation and analysis of other properties as well. That this is indeed true, has been concluded from the recent studies[144,197-202] of the variation of V, T_g and σ of several As based chalcogenide glass systems, viz., the $Ag_x(As_{0.4}Te_{0.6})_{100-x}$, $Cu_x(As_{0.4}Te_{0.6})_{100-x}$, $Cu_x(As_{0.4}Se_{0.3}Te_{0.3})_{100-x}$ and the $Ag_x(As_{0.4}Se_{0.3}Te_{0.3})_{100-x}$ glasses; the compositions of the various glasses in a specified system can be expressed in terms of the atomic percent, x, of the metallic additive (Cu or Ag in the four systems mentioned above).

Figure 12 and 13 show the V—x and T_g—x data for these glasses. Changes in slopes are observed in these dependencies at x values ranging from 1 to 3 atomic percent (depending on the system). Similarly, the σ of glasses up to x values between 1 to 3 atomic percent (in these various systems) are lower than that of the parent glass, while the σ of glasses with higher x values are higher than that of the parent glass[198-200].

The following are the conclusions[144,197-202] from the above studies. (i) in small concentrations, (generally up to 1 to 3 atomic percent), the metal atoms do not drastically affect the basic structure of the parent glass; (ii) assuming a uniform distribution of the metal in the matrix of the parent glass, the distance between the clusters of the metallic

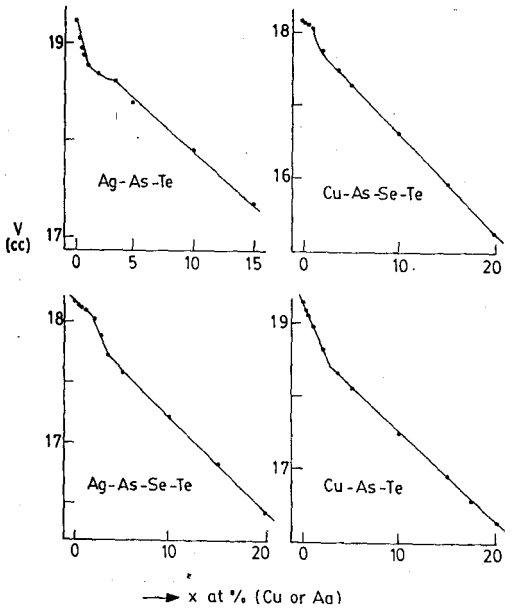

Fig. 12. V-x data[144,197,199,202] for Ag-As-Te, Cu-As-Te, Ag-As-Se-Te and Cu-As-Se-Te glasses

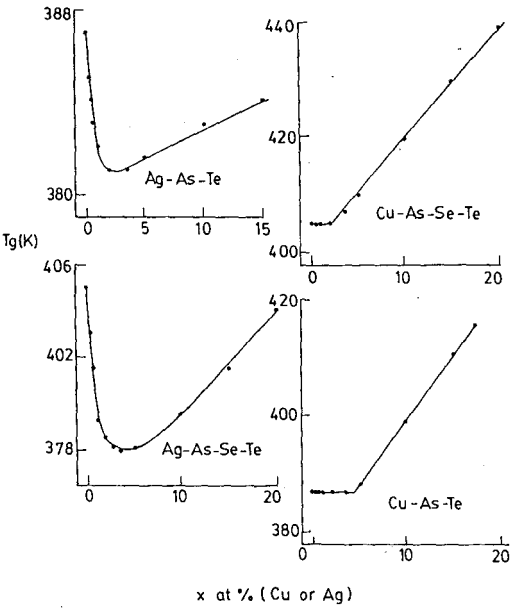

Fig. 13. Tg-x data[144,197,199,202] for Ag-As-Te, Cu-As-Te, Ag-As-Se-Te and Cu-As-Se-Te glasses.

atoms turns out to be greater than that of the medium range ordering (typically ~16 to ~18Å for chalcogenide glasses) for concentrations up to which the metallic atoms do not affect the structure of the parent glass. (iii) For higher concentrations, the metallic atoms affect the medium and short range ordering, by forming bonds with the elements of the parent glass; (iv) the properties of the resulting glasses can be rationalised by considering the formation of various structural units of the metal with the elements of the parent glass (e.g. formation of Ag_2Te structural units in the Ag-As-Te system, of the $CuAsSe_2$ and CuAsTe structural units in the Cu-As-Se-Te system , of the Cu_2Te structural units in the Cu-As-Te system and the Ag_2Te and the Ag_3AsSe_3 structural units in the Ag-As-Se-Te system). Another important conclusion from these studies is that it has pointed out the necessity of measuring also the variation of the activation energy for glass transition with composition in addition to the variation of T_g with composition, for a correct interpretation of the data in several systems.

ACKNOWLEDGEMENTS

The authors thank Dr. Singh, A. K., Head, Materials Science Division, N. A. L., and the present and the former Directors of N.A.L., for their encouragement and support throughout the course of this work.

REFERENCES

1. Ioffe, A. F., and Regal A. R., in : Progress in Semiconductors, Ed., G. R. Gibson (John Wiley, New York) 1960, vol. 4,

2. Lucovsky, G., Galeener, F. L., Geils, R. H., and Keezer, R. C., in : The structure of non-crystalline materials, Ed., P. H. Gaskell, (Taylor and Francis, London), 1977, p127.
3. Lucovsky, G., de Neufville, J. P., and Galeener, F.L., Phys. Rev., 1974, **B9**, 1591
4. Bienenstock, A., J. Non-Cryst. Solids, 1973, **11**, 447
5. Betts, F., Bienenstock, A., and Ovshinsky, S. R., J. Non-Cryst. Solids,1970, **4**, 554
6. Fawcett, R. W., Wagner, C. N. J., and Cargill III, G. S., J. Non-Cryst. Solids, 1972, **8-10,** 369
7. Betts, F., Beinenstock, A., and Bates Jr., C. W., J. Non-Cryst. Solids, 1972, **8-10**, 364
8. Fisher, G. B., Lindau, I., Orlowski, B. A., Spicer, W. E., Verhelle, Y., and Weaver, H. E., in : Proc. 5th. Int. Conf. Amorphous and Liquid Semiconductors, Garmisch - Partenkirchen, FRG, 1973, Eds. J. Stuke, and W. Brenig, (Taylor and Francis , London), 1974, vol.1, p 621
9. Boolchand, P., Key Engineering Materials, 1987, **13-15**, 131
10. Sudha Mahadevan and Giridhar, A., J. Non-Cryst. Solids, 1989, **110**, 118
11. S. R. Elliott, in: Physics of Amorphous Materials, (Longman, New York, 1983), Ch 3
12. Lucovsky, G., Galeener, F. L., Keezer, R. C., Geils, R. H., and Six, H. A., Phys. Rev., 1974, **B10**, 5134
13. Tronc, P., Bensousan, M., Brenac, A., and Sebenne, C., Phys. Rev., 1973, **B 8**, 5947
14. Feltz, A., Aust, H., and Blayer, A., J. Non-Cryst. Solids, 1983, **55**, 179
15. Lucovsky, G., Phys. Rev., 1977, **B 15**, 5762
16. Giridhar, A., Narasimham, P.S. L., and Sudha Mahadevan, J. Non-Cryst. Solids, 1980, **37**, 165
17. Narasimham, P.S. L., Giridhar, A., and Sudha Mahadevan, J. Non-Cryst.Solids, 1981, **43**, 365
18. Giridhar, A., Narasimham, P. S. L., and Sudha Mahadevan, J. Non-Cryst. Solids, 1981, **43**, 29
19. Feltz, A., Zickmuller, K., and Pfaff, H., Proc. Int. Conf. Amorphous and Liquid semiconductors (Edinburgh 1977) Ed., W. E. Spear (Centre for industrial consultancy and Liaison, Univ.of Edinburgh) 1977, p125
20. Giridhar, A., and Sudha Mahadevan, J. Non-Cryst. Solids, 1982, **51**, 305
21. Giridhar, A., and Sudha Mahadevan, J. Non-Cryst. Solids, 1990, **126**, 161
22. Mohan, R., Sudha Mahadevan, and Rao, K. J., Mats. Res. Bull., 1980, **15**, 22
23. Narasimham, P. S. L., Giridhar, A., and Sudha Mahadevan, J. Non-Cryst. Solids, 1981, **43**, 301
24. Giridhar, A., Sudha Mahadevan and Singh, A. K., Bull. Mats. Sci., 1986, **8**, 53.
25. Sudha Mahadevan, Giridhar, A., and Singh, A. K., J. Non-Cryst. Solids, 1986, **88**, 11

26. Varshneya, K., Sreeram, A. N., and Swiler, D. R., Phys. Chem. Glasses, 1993, **34**, 179
27. Cervinka, L., in : The structure of Non-Crystalline Materials, Eds., P. H. Gaskell, J. M. Parker, and E. A. Davis, (Taylor and Francis, London,1982), p164
28. Cremers, H., Mosel, B. D., Muller-warmuth, W., Frischat, W., and Braetsch V., Phys. Chem. Glasses, 1989, **30**, 79
29. Frischat, G. H., Borkmeior V., and Rosskamp, A., J. Non-Cryst. Solids, 1982, **50**, 263
30. Sreeram, A. N., Varshneya, K., and Swiler, D. R., J. Non-Cryst. Solids, 1991, **128**, 294
31. Sudha Mahadevan, Giridhar, A, and Singh, A. K., J. Non-Cryst. Solids, 1988, **103**, 179
32. Azoulay, R., Thieberg, H., and Brenac, A., J. Non-Cryst. Solids, 1975, **18**, 33
33. Myers, M. B., and Felty, E. J., Mat. Res. Bull, 1967, **2**, 715
34. Wright, A. C., Holmes, R. A., Grimley, D. I., Sinclair, R. N., Martin, S. W., Price, D. L., and Galeener, F. L., J. Non-Cryst. Solids, 1991, **129**, 213
35. Tanaka, K., Phys. Rev., 1989, **B 39**, 1270
36. Phillips, J. C., J. Non-Cryst. Solids, 1979, **34,** 153
37. Phillips, J. C., J. Non-Cryst. Solids, 1981, **43**, 37
38. Thorpe, M. F., J. Non-Cryst. Solids, 1983, **57**, 55
39. Phillips, J. C., and Thorpe, M. F., Solid State Comm., 1985, **53**, 699
40. Ota, R., Yamate, T., Soga, N., and Kunugi, M., J. Non-Cryst. Solids, 1978, **29**, 67
41. Halfpap, B., and Lindsay, S., Phys. Rev. Lett.,1986, **57**, 847
42. Boolchand, P., in : Physical properties of amorphous materials, Eds., D. Adler, B. B. Schwartz, and M. C. Steele, (Plenum, New York, 1985) p.221
43. Philip, J., and Madhusoodanan, K. N., Phys. Rev., 1988, **B 38**, 4127
44. Asokan, S., Parthasarathy, G., and Gopal, E. S. R., Phil. Mag., 1988, **B 57**, 49
45. Sudha Mahadevan and Giridhar, A., J. Non-Cryst. Solids, 1993, **162**, 294
46. Bresser, W., Boolchand, P., and Suranyi, P., Phys. Rev. Lett., 1986, **56**, 2493
47. Feng, X., Bresser, W.J., and Boolchand, P., Phys. Rev. Lett., 1997, **78**, 4422
48. Boolchand, P., in : Rigidity Theory and applications, Eds., M. F. Thorpe and P. M. Duxbury, (Plenum Press, New York, 1999)
49. Tsuchihashi, S., and Kawamoto, Y., J. Non-Cryst. Solids, 1971, **5**, 286
50. Maruno, S., and Noda, M., J. Non-Cryst. Solids, 1972, **7**, 1
51. Ota, R., Soga, N., and Kunugi, M., Yogyo-Kyokai-Shi, 1973, **81**, 36
52. Kawamoto, Y., and Tsuchihashi, S., J. Am. Ceram. Soc., 1971, **54**, 131
53. Prasad, M. R. N., Asokan, S., Parthasarathy, G., Titus S. S. K., and Gopal, E. S. R., Phys. Chem. Glasses, 1993, **34**,199

54. Lucovsky, G., in: Amorphous and Liquid Semiconductors, Eds., J. Stuke and W. Brenig, (Taylor and Francis, London) 1974, vol.2, 1099 (and references therein)

55. Nemanich, R. J,. Solin, S. A., and Lucovsky, G., Solid State Comm.,1973, **21**, 273.

56. Malaurent, J. C., Dixmier J., J. Non-Cryst. Solids, 1980, **35 & 36**, 1277

57. Cremers, H., Mosel, B. D., Muller-warmuth, W., and Frischat, G. H., J.Non-Cryst. Solids, 1984, **63**, 329

58. Petrovic, D. M., Khiminets, V. V., and Avaramov, M. I., Phys. Stat. Solidi, A 90 (1985) 151

59. Tenhover, M., Hazle, M. A., and Grasselli, R. K., J. Phys. C, 1985, **18**, 2025

60. Mamontova, T. N., Mukanov , Kh. K., Vingradova, G. Z., Maisahville, N. G., and Babievskaya, I. Z., Phys. Stat. Solidi , 1986, **A93**, 635

61. Koudelka, L., Pisarcik, M., Krylov, N. I., and Ananichev, V. A., J. Non- Cryst. Solids, 1987, **97 & 98**, 1271

62. Mikrut, J. M., and McNeil, I. E., J. Non-Cryst. Solids, 1989, **109**, 237

63. Yang, C. Y., Paesler, M. A., and Sayers, D. E., Phys. Rev., 1989, **B39**, 10342

64. Tverjanovich, A., Kruger, M., Soltwisch, M., and Quitmann, A. J., J. Non-Cryst. Solids, 1991, **130**, 236

65. Sudha Mahadevan, Giridhar, A., and Singh, A. K., J. Non-Cryst. Solids, 1988, **103**, 73.

66. Borisova, Z.U., in : Glassy semiconductors (Plenum, New York)1981.

67. Giridhar, A. and Sudha Mahadevan, J. Non-Cryst. Solids, 1991, **134**, 94

68. Giridhar, A. and Sudha Mahadevan, J. Non-Cryst.Solids, 1992, **151**, 245

69. Sudha Mahadevan and Giridhar, A., J. Non-Cryst. Solids, 1993, **152**, 42

70. Sudha Mahadevan and Giridhar, A., J. Mat. Sci., 1993, **28**, 1205

71. Sudha Mahadevan, and Giridhar, A., J. Non-Cryst. Solids, 1992, **143**, 52

72. Sudha Mahadevan, Giridhar, A., and Singh, A. K., J. Non-Cryst. Solids, 1994, **169**, 133.

73. Srinivasan, A, Madhusoodanan, K.N., Ganesan, R., and Gopal, E.S.R., Phys. Chem. Glasses, 1992, **33**, 206

74. Ruska, J., and Thurn, H., J. Non-Cryst. Solids, 1976, **22**, 277

75. Gan, F., Trans. Ind. Ceram. Soc., 1987, **46**, 33

76. Tille, U., Frischat, G. H., and Leers, K. J., Proc. 4^{th} Int. Conf. Phys. Non-cryst. Solids, Clausthal, Zellerfeld, 1976, Ed., G. H. Frischat (Trans Tech Publications, Switzerland), 1977, p.631

77. Myuller, R. L., Timofeeva, V. N., and Borisova, Z. U., in: Solid State Chemistry, Ed., Z. U. Borisova, (Consultants Bureau , New York) 1966, p46

78. Borisova, Z. U., and Pazin, A. V., ibid, p63

79. Savage, J. A., Webber, P. J., and Pitt, A. M., J. Mater. Sci., 1978, **13**, 859

80. Hayes, D. J., Rechtin, M. D., and Hilton, A. R., in : Ultrasonic Symposium Proc., 1974, Wisconsin, Ed., J. De Klerk, p . 502
81. Sudha Mahadevan, Giridhar, A., Narasimham, P. S. L., and Singh, A. K., J. Non-Cryst. Solids, 1984, **65**, 233
82. Giridhar, A., Sudha Mahadevan and Singh, A. K., Bull. Mat. Sci.,1984, **6**, 1001
83. Ito, Y., Kashida, S., and Murase., K., Solid State Comm., 1988, **65**, 449
84. Sudha Mahadevan, Giridhar, A., and Singh, A. K., J. Non-Cryst. Solids, 1983, **57**, 423
85. Tsiulyanu, D. I., Dragich, A. D., and Gumeniuk, N. A., J. Non-Cryst. Solids, 1993, **155**, 180
86. Borisova, Z. U., Kasatkin, B. E. and Kim, E. I., Inorg. Mat., 1973, **9**, 443
87. Singh, A. K., and Kennedy, G. C., J. Appl. Phys., 1975, **46**, 3861
88. Bruckhardt, W., Feltz, A., and Bussener, P., J. Non-Cryst. Solids, 1987, **89**, 273
89. Handbook of Chemistry and Physics (Chemical Rubber Co.) 52nd Edition
90. Reid, L. R., Phys. Chem. Glasses, 1968, **9**, 133
91. Webber, P.J., and Savage, J. A., J. Non-Cryst. Solids, 1976, **20**, 271
92. Krebs, H., and Ruska, J., J. Non-Cryst. Solids, 1974, **16**, 329
93. Stourac, L., Vasco, A., Srb, I., Musil, C., and Strba, F., Czech. J. Phys., 1968, **B18**, 1067
94. Carini, G., Cutroni, M., Federico, M., and Galli, G., J. Non-Cryst. Solids, 1984, **64**, 317
95. Soga, N., Kunugi, M., and Ota, R., J. Phys. Chem. Solids, 1973, **34**, 2143
96. Richter, H., and Breitling, G., Z. Naturforsch, 1951, **6a**, 721
97. Wu C. T., and Luo, H. L., J. Non-Cryst. Solids, 1975, **18**, 21
98. Trnovcova, V., Lezel, D., Marian, E., and M., Pavlikova, in Amorphous Semiconductors 1976, Proc. Int. Conf., Balatanfured, Hungary, Ed. Kosa Somogyi, p.493
99. Mohan, R., Panchapakesan, T., and Rao, K. J., Bull. Mat. Sci., 1981, **3**, 29
100. Shkolnkov, E. V., in : Solid State Chemistry , Ed., Z. U. Borisova, p. 132
101. Myuller, R. L., in : Electrical conductivity of Vitreous Substances, p. 133
102. Sawan, Y., Wakim, F. J., El Gabaly, M. and Rayees, M. L., J. Non-Cryst. Solids, 1980, **41**, 319
103. de Neufville, J. P., Moss, S. C., and Ovshinsky, S. R., J. Non-Cryst. Solids, 1973/74, **13**, 191
104. Kolomiets, B.T., Phys. Stat. Solidi, 1964, **7**, 359
105. Onari, S., Matsuichi, K., and Arai, T., J. Non-Cryst. Solids, 1986, **86**, 22
106. Hilton, A. R., and Hayes, D. J., J. Non-Cryst. Solids, 1971, **17**, 339
107. Savage, J. A., J. Non-Cryst. Solids, 1982, **47**, 101
108. Thompson, J.C., and Bailey, K.E., J. Non-Cryst. Solids, 1978, **27**, 161

109. Durcek, J., Hrivnak, L., Kolnik, S., Musil, C., and Strba, F., J. Non-Cryst. Solids, 1970, **4**, 66

110. Hach, C. T., Cerqua-Richardson, K., Varner, J. R., and LaCourse, W. C., J. Non-Cryst. Solids, 1997, **209**, 159

111. Loehman, R. E., Armstrong, A. J., Firestone, D. W., and Gould, R. W., J. Non-Cryst. Solids, 1972, **8 - 10**, 72

112. Feltz, A., Voigt, B., and Schlenzig, E., Amorphous and Liquid Semiconductors, Ed., J. Stuke, and W. Brenig, (Taylor and Francis, London, 1974) p 261

113. Feltz, A., Phole, M., Skil, M., and Herm, G., J. Non-Cryst. Solids, 1985, **69**, 271

114. Fischa - Colbrie, and Fuoss, P. H., J. Non-Cryst. Solids, 1990, **126**, 1

115. Kawamoto, Y., and Tsuchihashi, S., J. Amer. Ceram. Soc., 1971, **54**, 131

116. Cervinka L., and Hruby, A., Amorphous and Liquid Semiconductors, Ed., J. Stuke, and W. Brenig, (Taylor and Francis, London, 1974) p 431

117. Zhilinskaya, E. A., Lazukin, V. N., Valeev, N. Kh., and Obsalov, A. K., J. Non-Cryst. Solids, 1990, **124**, 48

118. Heo, J., and Mackenzie, J. D., J. Non-Cryst. Solids, 1989, **111**, 29

119. Ota, R., and Kunugi, M., J. Phys. Chem. Solids, 1977, **38**, 9

120. Cervinka, L., Smotlacha, O., and Tichi, L., J. Non-Cryst. Solids, 1987, **97 & 98**, 183

121. Andreichen, R., Nikiforova, M., Skordeva, E., Yurokova, L., Grigorovici, R., Manaila, R., Popescu, M., and Vancu, A., J. Non-Cryst. Solids, 1976, **20**, 101

122. Murano, S., and Noda, M., J. Non-Cryst. Solids, 1972, **7**, 1

123. Tauc, J., in : Amorphous and Liquid Semiconductors, Ed., J. Tauc, (Plenum Press, London) 1974, Ch. 4.

124. Doupovec, J., Thurzo, I., Barancok, D., and Shilo, V.P., Mat. Res. Bull., 1977, **12**, 119

125. Johnson Jr., R.T., and Quinn, R. K., J. Non-Cryst. Solids, 1978, **28**, 273

126. Cornett, J., and Rossier, D., J. Non-Cryst. Solids, 1973, **12**, 85

127. Seager, C. H., and Quinn, R. K., J. Non-Cryst. Solids, 1975, **17**, 386

128. Price, D. L., Misawa, M., Susman, S., Morrison, T. I., Shenoy, G. K., and Grimsditch, M., J. Non-Cryst. Solids, 1984, **66**, 443

129. Kolomietsova, S. E., Orlova, G. M., and Chalabyan, G. A., Inorg. Mat. 1981, **16**, 1046

130. Leadbetter, A.J., and Apling A.J., J. Non-Cryst. Solids, 1974, **15**, 250

131. Sreeram, A. N., Varsheneya, A. K., and Swiler, D. R., J. Non-Cryst. Solids, 1991, **128**, 294

132. Cornett, J. and Rossier, D., J. Non-Cryst. Solids, 1973, **12**, 61

133. Quinn, R. K., Mat. Res. Bull., 1974, **9**, 803

134. Phole, M., and Feltz, A., J. Non-Cryst. Solids, 1984, **69**, 283

135. Das, G.C., Bever, M.B., Dhimann, D.R., and Moss, S.C., J. Non-Cryst. Solids, 1972, **7**, 251

136. Sudha Mahadevan and Giridhar, A., Unpublished data

137. Eichhorn, U., and Frischat, G. H., J. Non-Cryst. Solids, 1978, **30**, 211

138. Farley, J. M., and Saunders, G. A., J. Non-Cryst. Solids, 1975, **18**, 417

139. Savage, J. A., Webber, P. J., and Pitt, A. M., Infrared Phys., 1980, **20**, 313

140. Mitkova - Vassileva, M., and Boncheva - Mladenova Z., Amorphous and Liquid Semiconductors, 76, Proc. Int. Conf., Balatonfured, Hungary, Ed. Kosa Somogyi, p. 455

141. Giridhar, A. and Sudha Mahadevan, J. Non-Cryst. Solids, 1991, **134**, 211

142. Vengal,T. N., and Kolomiets, B. T., Sov. Phys. Tech. Phys., 1957, **2**, 231

143. Thornburg, D. D., J. Elec. Mats., 1973, **2**, 495

144. Sudha Mahadevan and Giridhar, A., J. Non-Cryst. Solids, 1997, **221**, 281

145. Carcely, C., and Houphouet-Boigny, D., J. Non-Cryst. Solids, 1986, **86**, 271

146. Moynihan, C. T., Easteal, A. J., Wilder, J., and Tucker, J., J. Phys. Chem., 1974, **78**, 2673

147. Crichton S. N., and Moynihan, C. T., J. Non-Cryst. Solids, 1988, **99**, 413

148. de Neufville, J. P., and Rockstad H. K., in : Amorphous and Liquid Semiconductors, Eds., J. Stuke, and W. Brenig, vol 1, (Taylor and Francis, London, 1974) p 419

149. Tichi, L., and Ticha, H., J. Non-Cryst. Solids, 1995, **189**, 141

150. Heuer, A., and Spiess, H.W., J. Non-Cryst. Solids, 1994, **176**, 294

151. Chen, H. S., J. Non-Cryst.Solids, 1978, **27**, 257

152. Shelby, J. E., J. Non-Cryst.Solids, 1979, **34**, 111

153. Colmenero, J., and Barandiaran, J. M., J. Non-Cryst.Solids, 1978, **30**, 263

154. Macmillan, J. A., J.Phys.Chem., 1965, **42**, 3497

155. Kissinger, H. E., J. Res. Nat. Bur. Stand., 1956, **57,** 217

156. Hartke, J. L., Phys. Rev., 1962, **125**, 177

157. Mott, N. F., and Davis, E. A., Electronic processes in materials (Clarendon Press, Oxford) 1971.

158. Sudha Mahadevan, Giridhar, A., and Rao, K. J., J. Phys.C (Solid State Physics) 1977, **10**, 4499

159. Sudha Mahadevan, and Giridhar, A., J. Mats. Sci., 1994, **29**, 3837

160. Kim, E. I., and Orlova, G. M., Zh. Prikl. Khim., 1974, **47**, 989

161. Economou, E. N., in Amorphous and Liquid Semiconductors, Ed., J. Tauc, (Plenum Press, London and New York) 1974, ch. 3

162. Donovan, T. M., Spicer, W. E., Bennett, J. M., and Ashley, E. J., Phys. Rev., (1970), **B2**, 397

163. Fritzche, H., in Amorphous and Liquid Semiconductors, Ed., J. Tauc, (Plenum Press, London and New York) 1974, ch. 5

164. Sudha Mahadevan and Rao, K. J., J. Non-Cryst. Solids, 1979, **34**, 53

165. Emin, D., Electronic and structural properties of amorphous semiconductors, Ed., Le Comber, P. G., Mort, J., (Academic Press, London) 1971, Ch.7.

166. Rockstad, H. K., Flasck, R., and Iwasa, S., J. Non-Cryst. Solids, 1972, **8-10**, 326

167. Arnoldusson, C.A., Menezes, C. A., Nagakawa, Y., and Bube, R. H., Phys. Rev., 1974, **89**, 3377

168. McSkimin, H. J., J. Acoust. Soc. America, 1961, **33**, 12

169. May Jr., J. E., IRE Natl. Conv. Rec., 1958, **6** (pt.2), 134

170. Papadakis, E. P., J. Appl Phys., 1964, **35**, 1474

171. Philip, J. Bulletin of Electrochemistry, 1996, **12**, 678

172. Spear, W.E., and LeComber, P. G., Phil. Mag., 1976, **33**, 935

173. Paul, W., Lewis, A. J., Connell, G. A. N., Moustakas, T. D. , Solid State. Comm., 1976, **20**, 969

174. Araki, M., and Zaki, H., Solid State Comm., 1976, **18**, 1603

175. Nath, P. Barthwal, S. K., and Chopra, K. L., ibid, 1975, **16**, 301 and 723

176. Ovshinsky, S. R., in Amorphous and Liquid Semiconductors (Proc. 7^{th}. Int. Conf. on Amor. and Liq. Semicond., Edinburgh, 1977) Ed., Spear, W. E., (Centre for industrial Consultancy and Liaison, University of Edinburgh,1977), p.519.

177. Flasck, R., Izu, M., Sapru, K., Anderson, T., Ovshinsky, S. R., and Fritzsche, H., in Amorphous and Liquid Semiconductors (Proc. 7^{th}. Int. Conf. on Amor. and Liq. Semicond., Edinburgh, 1977) Ed., Spear, W. E., (Centre for industrial Consultancy and Liaison, University of Edinburgh,1977), p.524.

178. Arai, K., Kuwahata, T., Namikawa, H., and Saito, S., Jpn. J. App. Phys., 1972, **11**, 1080

179. Kosek, F., Cimpl, Z., Mikhalov, E.A., Karpova, E.A., J. Non-Cryst. Solids, 1986, **86**, 265

180. Ticha, H., Tichy, L., and Klikorka, J., J. Mats. Res., 1987, **2**, 361

181. Kitao, M., Senda, M., Takano, Y., and Yamada, S., J. Non-Cryst. Solids, 1991, **127**, 36.

182. Fraser, M. I., and Owen, A. E., J. Non-Cryst. Solids, 1983, **59&60**, 1031

183. Kolomiets, B. T., Rukhlyadev, Yu. V., and Shilo, V. P., J. Non-Cryst. Solids, 1971, **5**, 389 and 402

184. Pfister, G., and Taylor, P. C., J. Non-Cryst. Solids, 1980, **35&36**, 793 (and references therein)

185. Owen, A. E., and Marshall, J. M., in: Amorphous and Liquid Semiconductors (Proc. 7^{th}. Int. Conf. on Amor. and Liq. Semicond., Edinburgh, 1977) Ed., Spear, W. E., (Centre for Industrial Consultancy and Liaison, University of Edinburgh,1977), p.529.

186. Nagels, P., in : Amorphous Semiconductors, Topics in Applied Physics, Vol. 36, Ed., M. H. Brodsky, (Springer - Verlag, Berlin) 1979, Ch. 5.

187. Mott, N. F., Davis, E. A., and Street, R. A., Phil Mag., 1975, **32**, 961

188. Kastner, M., Adler, D. and Fritzche, H., Phys. Rev. Lett., 1976, **37**, 1504

189. Fritzche, H., in: Amorphous and Liquid Semiconductors (Proc. 7th. Int. Conf. on Amor. and Liq. Semicond., Edinburgh, 1977) Ed., W. E. Spear, (Centre for Industrial Consultancy and Liaison, Univ. Edinburgh,1977), p.3

190. Street, R. A. and Lucovsky, G., Solid State Comm., 1979, **31,** 289

191. Fritzche, H., and Kastner, M., Phil. Mag., 1979, **37B**, 285

192. Pfister, G., Morgan, M., and Liang, K. S., Solid State Comm., 1979, **30**, 277

193. Tohge, N., Minami, T., and Tanaka, M., J. Appl. Phys., 1980, **51**, 1048

194. Tohge, N., Yonesaki, Y., and Minami, T ., J. Appl. Phys., 1980, **58**, 4225

195. Bhatia, K. L., Malik, S. K., Kishore, N. and Singh, S. P., Phil. Mag.,1992, **B 66**, 587

196. Malik, S. K., Bhatia, K. L., Bhatnagar, V. K., Phil. Mag., 1991, **B 63**, 573

197. Sudha Mahadevan and Giridhar, A., J. Non-Cryst. Solids, 1996, **197**, 219

198. Giridhar, A., and Sudha Mahadevan, J. Non-Cryst. Solids, 1996, **197,** 228

199. Giridhar, A., and Sudha Mahadevan, J. Non-Cryst. Solids, 1998, **238**, 225

200. Giridhar, A., and Sudha Mahadevan, J. Mat. Sci., 1999, **34**, 1281

201. Giridhar, A., and Sudha Mahadevan, J. Non-Cryst. Solids, 1999, **248,** 253

202. Sudha Mahadevan and Giridhar, A., J. Non-Cryst. Solids, 1999, **258**, 207